SYNLETTE
Spotlight 51

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Cerium(III) Chloride Heptahydrate: CeCl₃·7H₂O

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Introduction

Few areas of synthetic chemistry have witnessed a growth as explosive as that brought about by the application of lanthanide reagents to organic synthesis. Cerium(III) chloride heptahydrate¹ is a commercially available lanthanide reagent which is water tolerant, non-toxic, easy to handle, inexpensive and can be used without further purification.

Abstracts

A) Luche² introduced this reagent in 1978 for the selective 1,2 reduction of enones. Since the preparation of organocerium compounds by Imamoto and co-workers³ in early 1980’s these are now widely applied as the reagent of choice to facilitate nucleophilic addition reactions. Recently, Bartoli and co-workers⁴ demonstrated the reactivity of CeCl₃·7H₂O in combination with NaI for several organic transformations.

B) Cerium(III) chloride was shown to catalyze the Michael addition⁵ of 1,3 dicarbonyl compounds to α,β-unsaturated ketones and α,β-unsaturated aldehydes in the presence of NaI. The catalyst system can be easily separated from the reaction mixture and it can be reused without an appreciable loss of activity. The reactions can also be performed without solvents under microwave irradiation.⁶

C) Cerium(III) chloride is a novel reagent for the nonaqueous selective conversion of dioxolane to carbonyl compounds.⁷ Similarly, CeCl₃·7H₂O–NaI in acetonitrile has been recently reported for the selective deprotection of the tert-butyl esters in the presence of N-Boc protecting group.⁸

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D) Highly regioselective ring opening of epoxides and aziridines has been carried out using cerium(III) chloride to synthesize the corresponding chlorohydrins,11 iodohydrins,11 1,2-azidoalcohols,12 1,2-aminoalcohol,13 chloroamines,14 iodoamines11 and 1,2-azidoamines.12

E) Cerium(III) chloride has been used as a mild Lewis acid, and efficient catalyst for the deprotection of alcohol protecting groups such as MEM,14 Tr,15 TBDMS,16 allyl,17 prenyl,18 Me18 and PMB.19

A simple and efficient method for the conversion of alcohols into alkyl iodides20 using CeCl3 –SnCl2, providing [3+4] cycloadducts via the oxyallyl cation intermediate.21

F) αβ-Dibromo ketones react with 1,3-dienes in the presence of CeCl3–SnCl2, providing [3+4] cycloadducts via the oxyallyl cation intermediate.21

G) Organocerium reagents22 are generated in situ by transmetalation reactions from organolithium23 or organomagnesium reagents.4 Organocerium reagents are highly oxophilic and significantly less basic than their RLi and RMgBr counterparts.

References